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STRUCTURAL INVESTIGATION OF LAC RESIN—II*

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Abstract—The three fractions of lac resin viz., hard resin I, hard resin II and soft resin have been cleaved with hydriodic acid followed by deiodination. The products were separated into fatty acids and terpene acids. The former have been studied by GLC and data on the nature and distribution of the chain lengths and their relative amounts were thus obtained. Cleavage of the different fractions of the resin with hydrogen chloride followed by alkaline hydrolysis gave the total aleuritic acid quantitatively. Based on the above results, the possibility of the presence of alkali stable linkages in lac resin and the amount of aleuritic acid liberated only by acid cleavage have been determined.

LAC resin has been considered to contain primarily ester type linkages. However, various conditions of alkaline hydrolysis[1] yield only ~ 20% of aleuritic acid (9,10,16-trihydroxypalmitic acid). To examine whether part of the aleuritic acid is involved in alkali stable linkages, the resin was degraded under acidic conditions.

Model experiments on aleuritic acid

An investigation of the action of halogen acids on aleuritic acid has been undertaken as a preliminary to extending the reaction to lac resin itself. The action of hydrogen chloride on *vicinal* glycols in general and the stereochemical implications involved, using 9,10-dihydroxystearic acid, have been investigated in detail.[2-4]

TABLE 1. ACTION OF HALOGEN ACIDS*

HX	Reaction conditions	Products
1. Dry HCl gas in AcOH	110° for 3 hr	i *erythro* acid ii *trans* epoxide
2a Dry HBr gas in AcOH	Room temp. for 16 hr	i *erythro* acid ii *trans* epoxide
b Aqueous HBr in AcOH	115° for 2 hr	i *erythro* acid (minor) ii fraction of monohydroxy acids iii fraction of dihydroxy acids
3. Aqueous HI in AcOH	100° for 1 hr	i fraction of monohydroxy acids ii fraction of dihydroxy acids

* Starting material *threo*-aleuritic acid. Alkaline hydrolysis reflux temp in all cases

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* Structural Investigation of Lac Resin-Part-I, Chemical Studies on Hard Resin, *Indian J. Chem.* in press.

[1] R. Madhav, T. R. Seshadri and G. B. V. Subramanian, *Curr. Sci.* **32**, 151 (1963).

[2] D. Atherton and T. P. Hilditch, *J. Chem. Soc.* 204 (1943).

[3] D. Swern, *J. Am. Chem. Soc.* **70**, 1235 (1948).

[4] G. King, *J. Chem. Soc.* 387 (1942); 1820 (1949).

According to Swern[3] an odd number of inversions take place during the conversion of *threo* into *erythro* form, through reaction with hydrogen chloride followed by alkaline hydrolysis.

A series of experiments have now been carried out using various conditions on aleuritic acid using hydrogen chloride, hydrogen bromide and hydrogen iodide followed by alkaline hydrolysis. The presence of an ω-hydroxyl group is a special feature in the case of aleuritic acid. The results are summarized in Table 1. The reactions with hydrogen chloride and hydrogen iodide have been applied for the fission of the resin.

Fission of the resin with hydriodic acid

The hard resins I, II and soft resin were fissioned with hydriodic acid followed by deiodination and the products separated into fatty acids and terpene acids. The fatty acid fraction was chromatographed on a column of neutral alumina and was shown to be free from hydrocarbons and alcohols. The acids were then converted into their methyl esters and studied by GLC (Fig. 1). C_{16}-Acids were found to be maximum in hard resin I and progressively decreased to a minimum in soft resin.

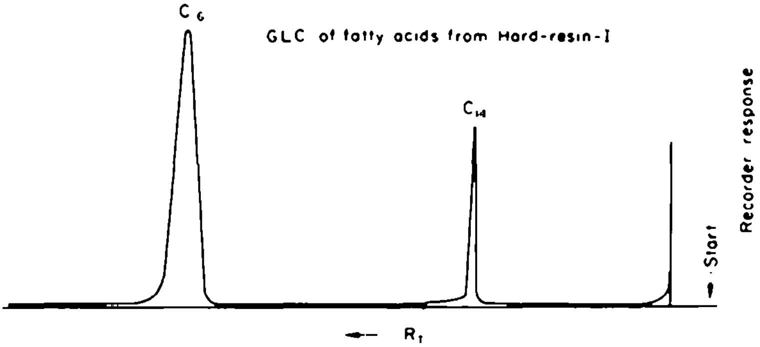
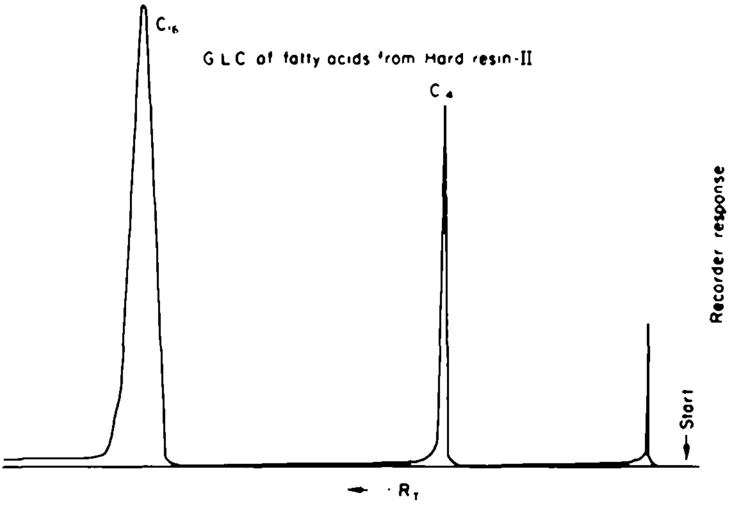
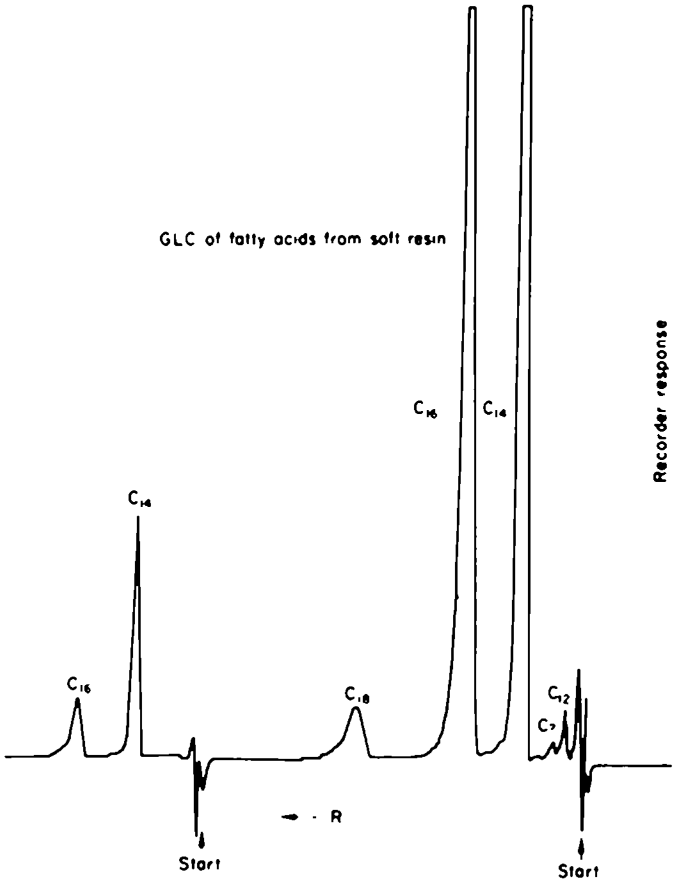


FIG 1. GLC charts.





On the other hand C_{14}-acids increased to a maximum in soft resin. The following Table 2 indicates the relative abundance.

Fission of the resin with hydrogen chloride

Since the *vicinal* glycol system of aleuritic acid is retained in this reaction (cf. Table 1), the resin was fissioned with hydrogen chloride followed by alkaline hydrolysis. The ether insoluble *erythro* aleuritic acid was readily separated from all other products including the terpene acids which dissolve in ether. Table 3 summarizes the yields of *erythro* acid from different types of lac.

TLC of the ether insoluble product showed the presence of only *erythro* aleuritic acid and no *threo* acid and that of the ether soluble fraction indicated the absence of both *erythro* and *threo* aleuritic acids but showed the presence of butolic acid.

Discussion of the results

Aleuritic acid and the terpene acid, jalaric acid[5] are the building blocks of the hard resin together with a minor contribution from butolic acid. Hard resin is the important part of shellac and the desirable properties of shellac are associated with it.

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[5] R. G. Khurana, M. S. Wadia, V. V. Mhaskar and Sukh Dev, *Tetrahedron Letters* 513 (1964).

TABLE 2.

Resin	C_{12}	C_{14}	C_{16}	C_{18}
Hard resin-I	·	1	6	--
Hard resin-II		1	5	
Soft resin	Trace	30	20	1

TABLE 3.

Types of lac	% of *erythro* acid by HCl reaction alkaline hydrolysis	% of *threo* acid by direct alkaline hydrolysis
Hard resin-I (from palas seedlac)	30–35%	20
Hard resin-II (from palas seedlac)	25	---
Soft resin (from palas seedlac)	10–12	
Platina shellac	30–35	
Lemon shellac	40	
Angelo superblonde shellac	40	20–22

Brief notes[1-6] on the role of aleuritic acid in the resin formation were published earlier and the possible presence of alkali stable linkages indicated. This conclusion was later supported by Gunstone *et al.*[7] who isolated a small quantity of aleuritic acid dimer formed through ether linkages. They however have based their investigations on the unfractionated shellac and have reported the isolation of $\sim 22\%$ aleuritic acid by alkaline hydrolysis. The remainder has been described as "polymeric acids" ($\sim 32\%$). A large number of minor fatty acids reported by them have no significant bearing on the hard resin formation since these acids are largely eliminated in soft resin during fractionation.

Most of the data of earlier workers on the extent of aleuritic acid, the main fatty acid component of the hard resin has been based either on speculation or ambiguous methods of estimation. The present work shows that no more than 40% of aleuritic acid can be present in the resin. This conclusion is based on the actual isolation of *erythro*-aleuritic acid (~ 35–40%) from different types of lac and also the isolation of total palmitic acid obtainable by hydriodic acid cleavage followed by deiodination. However, only $\sim 20\%$ of *threo*-aleuritic acid is liberated by alkaline hydrolysis. The remainder (~ 15–20%) is susceptible only to acid cleavage. This indicates the presence of alkali stable linkages to a substantial degree, a fact not recognized so far though Gunstone *et al.* report the isolation of a dimer of aleuritic acid in minor quantities. The aleuritic acid not liberated by alkaline hydrolysis should also have the *threo* configuration, since the total aleuritic acid obtained after reaction with hydrogen chloride was entirely *erythro* acid. During the course of the fission, the *threo* acid of the hard resin apparently has undergone an odd number of inversions as in the case of free *threo*-aleuritic acid.

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[6] R. Madhav, T. R. Seshadri and G. B. V. Subramanian, *Curr. Sci.* 33, 264 (1964).

[7] W. W. Christie, F. D. Gunstone, H. G. Prentice and S. C. Sen Gupta, *J. Chem. Soc.* 5833 (1964).

EXPERIMENTAL

Action of hydrogen chloride on threo-aleuritic acid. A stream of dry HCl gas was passed into a soln of *threo*-aleuritic acid (10 g) in glacial AcOH (50 ml) at 110–115° for 3 hr. The HCl and AcOH were removed from the reaction mixture under reduced press and the residue extracted with AcOEt. On removal of the solvent a viscous residue was obtained which was hydrolysed by heating under reflux with 10% NaOH aq (500 ml) for 3 hr. The soln was cooled and acidified with ice-cold dil HCl. The solid that separated was filtered off, washed and dried (7·0 g). It was then separated into a hot benzene soluble fraction and an insoluble fraction m.p. 125–127°. The benzene insoluble fraction readily crystallized from MeOH or AcOEt m.p. 125–127°. (Found: C, 62·7; H, 11·1; $C_{16}H_{32}O_5$ requires: C, 63·2; H, 10·5%.) It was identified as *erythro*-aleuritic acid by oxidation with alkaline $KMnO_4$ into the dicarboxylic acid and by periodate fission to show the retention of the *vic*-glycol group.

The benzene soluble fraction, on repeated crystallization from AcOEt followed by acetone–pet. ether at 0° gave clusters of tiny needles, m.p. 75° (Found: C, 67·6; H, 11·2; $C_{16}H_{30}O_4$ requires: C, 67·1; H, 10·6%). It was shown to be 16-hydroxy-*trans*-9,10-epoxyhexadecanoic acid by the following experiment.

Acetolysis. The above compound (50 mg) was refluxed with glacial AcOH (1 ml) for 1½ hr on an oil-bath. The reaction mixture was concentrated under reduced press and the residue hydrolysed by heating under reflux with 20% NaOH aq (2 ml) for 1 hr. The solid obtained on acidification was filtered off, washed and dried. It crystallized from MeOH, m.p. 125–127° and was identical with *erythro*-aleuritic acid.

Hydrogenation. The hydrogenation was carried out using Pd-C in a Parr hydrogenater, with EtOH as solvent. The product, m.p. 85–86° did not correspond to either pure 9,16-or 10,16-dihydroxyhexadecanoic acids, as expected.

Action of hydriodic acid on threo-aleuritic acid. A soln of aleuritic acid (5 g) in glacial AcOH (15 ml) was heated with freshly distilled constant boiling HI (25 ml, *d.* 1·7) at 100° for 1 hr. The reaction mixture was poured over crushed ice and extracted with AcOEt. The extract was washed with 5% $NaHSO_3$aq, then with water, dried and distilled. The residual oil (6·9 g) was hydrolysed with NaOH aq as described and the resulting solid after acidification (4·1 g) was separated into a pet. ether soluble fraction analysing for a monohydroxy acid. (Found: C, 70·8; H, 11·6; $C_{16}H_{30}O_3$ requires: C, 71·1; H, 11·2%) and a benzene soluble fraction analyzing for a dihydroxy acid. (Found: C, 66·5; H, 10·7; $C_{16}H_{32}O_4$ requires: C, 66·6; H, 11·2%.) No *erythro*-aleuritic acid or the corresponding *epoxide* were obtained in this case.

Similar experiments were carried out with HBr and the results are given in Table 1.

Hydriodic acid fission of hard resin-I. To a soln of hard resin-I (10 g) in glacial AcOH (30 ml), constant boiling HI (50 ml; 58%, sp gr. 1·7) and red phosphorus (0·5 g) were added. The mixture was heated at 110–115° for 2 hr, poured over crushed ice and extracted with AcOEt (50 ml × 4). The organic layer was washed with a soln of 5% $NaHSO_3$aq, and finally with water, dried (Na_2SO_4) and the solvent removed leaving a dark brown oil (10·1 g) which consisted of iodinated fatty acids and terpene acids. Two methods were used for their separation. In one, this iodinated product was separated into a $NaHCO_3$aq soluble fraction (terpene acids) and an insoluble fraction (fatty acids). These were then reduced separately to the parent acids. Another method was developed later and found to be better. In this, the mixture of iodinated oil was reduced and the fatty acids separated by soln in pet. ether.

Reduction of the dark brown oil. To a soln of the above oil (10·1 g) in glacial AcOH (70 ml), freshly prepared Zn-Hg (44 g) was added and the mixture heated on a water bath for 4 hr, with the addition of conc HCl (70 ml) in small quantities. The soln was cooled in crushed ice, with separation of a colourless waxy solid. This was removed by filtration and the filtrate extracted with AcOEt, washed free of AcOH, dried (Na_2SO_4) and the solvent removed. This was combined with the solid obtained earlier and extracted with warm pet. ether to give the fatty acids (3·2 g) and the insoluble fraction consisted of terpene acids (1·5 g).

Hydriodic acid fission of hard resin-II and soft resin. A similar series of reactions on hard resin II and soft resin gave the respective components. Hard resin-II (5 g) gave fatty acids (1·5 g) and a small amount of terpenes (0·8 g). Soft resin (5 g) gave fatty acids (2 g) and terpene acids (1 g). No further work was done on the terpene fractions.

Fractionation of fatty acids. The fatty acids (3 g) were passed through a column of neutral alumina (100 g, 31 × 1·3 cm). Elution was done with pet. ether, $CHCl_3$–EtOH, EtOH and finally with EtOH–AcOH (9:1 v/v). The main fraction eluted with EtOH–AcOH was concentrated under reduced press, diluted with water and acidified with dil HCl to decompose any aluminium salts. The solid (2·95 g) obtained was filtered off, washed with water and dried. The IR spectrum showed the absence of double bond and ester functions.

Gas-liquid chromatography of fatty acid methyl esters. The methyl esters of fatty acids were prepared with diazomethane. In the case of hard resin-I and hard resin-II, GLC was done on a column of Apiezon L (Q), (Golay column; 50 meters) at a temp of 190° with He as carrier gas at a flow rate of 375 cc/min. In the case of soft resin, GLC was done on a column of polyethylene glycol adipate at a temp of 185° with argon as carrier gas at a flow rate of 70 cc/min. Hard resin-I and hard resin-II showed only the presence of C_{14} and C_{16} chain lengths while soft resin showed C_{12}, C_{14}, C_{16} and C_{18} chain lengths. The GLC chromatograms are shown in Fig. 1. The relative ratios have been indicated earlier. (Table 2).

*Chloro-resin from hard resin-*I. To a soln of hard resin-I (10 g) in glacial AcOH (50 ml) a stream of dry HCl gas was passed for 6 hr, while the mixture was kept at 110–115°. AcOH was removed under reduced press, leaving a brownish viscous residue (14·3 g) which gave a positive test for chlorine.

Alkali hydrolysis of chloro-resin. The above residue (14·3 g) dissolved in 10% NaOH (500 ml) was refluxed for 3 hr, cooled and acidified with ice cold dil HCl, when a brown amorphous solid was obtained. It was filtered off, washed with water and macerated with ether. The residue crystallized from AcOEt (charcoal) as shining rhombic crystals (3·5 g), m.p. 119–120°. Recrystallization from AcOEt gave glistening clusters, m.p. 125–127°. (Found: C, 62·7; H, 11·0. $C_{16}H_{32}O_5$ requires: C, 63·1; H, 10·5%.) Mixed m.p. with a sample of *erythro*-aleuritic acid was undepressed.

TLC of the ether soluble gummy mass on silica gel plates impregnated with boric acid (5·6% soln) in the solvent system $CHCl_3$ MeOH (96:4) showed the presence of a large amount of butolic acid and a trace of *erythro*-aleutritic acid. The other spots were unidentified.

Similar cleavage has been carried out on hard resin-II, soft resin and different types of shellac. The yields of aleuritic acid from these have been given in Table 3.

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